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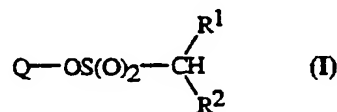
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(21) International Application Number: PCT/US94/06346 (22) International Filing Date: 10 June 1994 (10.06.94) (30) Priority Data: 08/078,530 17 June 1993 (17.06.93) US (60) Parent Application or Grant (63) Related by Continuation US 08/078,530 (CIP) Filed on 17 June 1993 (17.06.93) (71) Applicant (for all designated States except US): DUNLENA PTY LTD. [AU/AU]; 168 Walker Street, North Sydney, NSW 2060 (AU). (72) Inventor; and (75) Inventor/Applicant (for US only): FINKELSTEIN, Bruce, Lawrence [US/US]; 204 Valley Stream Drive, Newark, DE 19702 (US). (74) Agents: COSTELLO, James, A. et al.; E.I. Du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: AU, BB, BG, BR, BY, CA, CN, CZ, FI, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LV, MD, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report.	

(54) Title: ARTHROPODICIDAL SULFONATES

(57) Abstract

Arthropodicial and nematocidal compounds, compositions and use of compounds having formula (I) wherein Q, R¹ and R² are as defined in the text.



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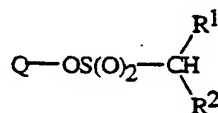
TITLE

ARTHROPODICIDAL SULFONATES

U.S. Patents 4,791,127, U.S. 4,987,141, U.S. 3,818,102 and U.S. 3,966,754 disclose insecticidal sulfonates. The instant invention is distinguished from these patents
5 in the unique character of the R¹ and R² substitution.

SUMMARY OF THE INVENTION

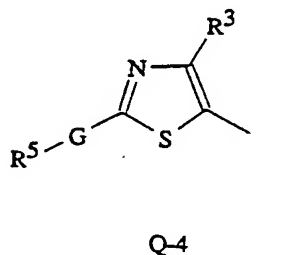
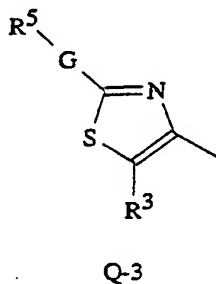
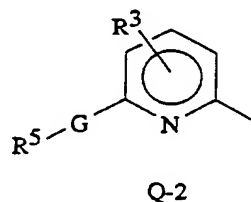
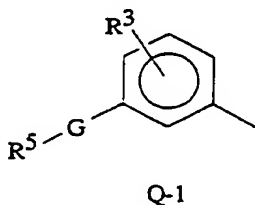
This invention pertains to compounds of Formula I, including all geometric and stereoisomers, agriculturally suitable salts thereof, agricultural compositions containing them and their use to control arthropods in both agronomic and nonagronomic
10 environments. The compounds are:



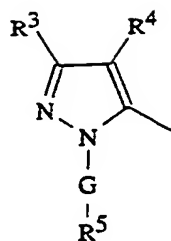
I

wherein:

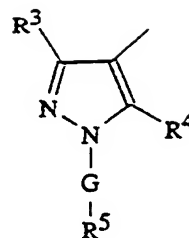
15 Q is selected from the group



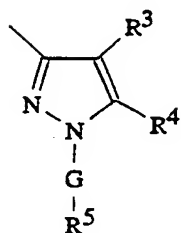
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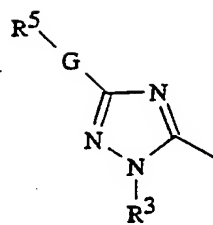
Q-5



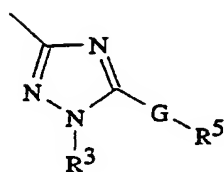
Q-6



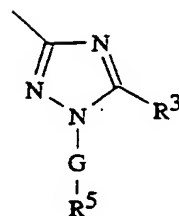
Q-7



Q-8

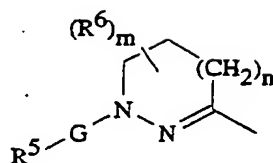


Q-9



Q-10

and



Q-11

5

R^1 is selected from the group CN, NO_2 , OR^7 , $C(O)R^7$, $C(O)OR^7$, $C(O)N(R^7)R^8$, SR^7 , $S(O)R^7$, $S(O)_2R^7$ and $S(O)_2N(R^7)R^8$;

R^2 is selected from the group H, C_1-C_3 alkyl, CN, $C(O)OR^7$ and $C(O)N(R^7)R^8$;

R^3 and R^4 are independently selected from the group C_1-C_6 alkyl, C_1-C_6 haloalkyl,

10 C_1-C_6 alkoxy, C_1-C_6 haloalkoxy, C_1-C_6 alkylthio, C_1-C_6 haloalkylthio,

C_1-C_6 alkylsulfinyl, C_1-C_6 haloalkylsulfinyl, C_1-C_6 alkylsulfonyl,

C_1-C_6 haloalkylsulfonyl, C_2-C_6 alkenyl, C_2-C_6 alkenyloxy, C_2-C_6

haloalkenyl, C_2-C_6 haloalkenyloxy, C_2-C_6 alkenylthio,

C_2-C_6 haloalkenylthio, C_2-C_6 alkenylsulfinyl, C_2-C_6 haloalkenylsulfinyl,

15 C_2-C_6 alkenylsulfonyl, C_2-C_6 haloalkenylsulfonyl, C_2-C_6 alkynyl, C_2-C_6

- alkynyloxy, C₂-C₆ alkynyloxy, C₂-C₆ haloalkynyl, C₂-C₆ alkynylthio, C₂-C₆ haloalkynylthio, C₂-C₆ alkynylsulfinyl, C₂-C₆ haloalkynylsulfinyl, C₂-C₆ alkynylsulfonyl, C₂-C₆ haloalkynylsulfonyl, C₃-C₆ cycloalkyl, C₃-C₆ halocycloalkyl, C₃-C₆ cycloalkoxy, C₃-C₆ halocycloalkoxy, C₃-C₆ cycloalkylthio, C₃-C₆ halocycloalkylthio, C₃-C₆ cycloalkylsulfinyl, C₃-C₆ halocycloalkylsulfinyl, C₃-C₆ cycloalkylsulfonyl, C₃-C₆ halocycloalkylsulfonyl, C₅-C₆ cycloalkenyl, C₅-C₆ halocycloalkenyl, C₅-C₆ cycloalkenyloxy, C₅-C₆ halocycloalkenyloxy, C₅-C₆ cycloalkenylthio, C₅-C₆ halocycloalkenylthio, C₅-C₆ cycloalkenylsulfinyl, C₅-C₆ halocycloalkenylsulfinyl, C₅-C₆ cycloalkenylsulfonyl and C₅-C₆ halocycloalkenylsulfonyl each optionally substituted with a substituent selected from the group R⁹; H; CN; NO₂; halogen; C₂-C₆ alkylcarbonyl; C₂-C₆ haloalkylcarbonyl; C₂-C₆ alkoxycarbonyl; C₂-C₆ haloalkoxycarbonyl; C(O)N(R¹⁰)R¹¹; C(S)N(R¹⁰)R¹¹; S(O)₂N(R¹⁰)R¹¹; C(O)H; N(R¹⁰)R¹¹; phenyl optionally substituted with 1 or 2 substituents independently selected from the group W; benzyl optionally substituted with 1 or 2 substituents independently selected from the group W;
- R⁵ is selected from the group C₁-C₆ alkyl, C₃-C₆ cycloalkyl, C₂-C₆ alkenyl and C₂-C₆ alkynyl each optionally substituted with a substituent selected from the group R⁹; C₁-C₆ haloalkyl; C₃-C₆ halocycloalkyl; C₂-C₆ haloalkenyl; C₂-C₆ haloalkynyl; C₄-C₇ cycloalkylalkyl; C₄-C₇ halocycloalkylalkyl; and N(R¹⁰)R¹¹;
- R⁶ is selected from the group halogen, CN, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₃-C₆ cycloalkyl, C₂-C₆ alkenyl, C₂-C₆ alkynyl, C₁-C₆ alkoxy, C₃-C₆ halocycloalkyl, C₂-C₆ haloalkenyl, C₂-C₆ haloalkynyl, C₄-C₇ cycloalkylalkyl, C₂-C₆ alkoxycarbonyl, N(R¹⁰)R¹¹, C(O)N(R¹⁰)R¹¹ and phenyl optionally substituted with 1 or 2 substituents independently selected from the group W;
- R⁷ and R⁸ are independently selected the group C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₃-C₆ cycloalkyl, phenyl optionally substituted with 1 or 2 substituents independently selected from the group W and benzyl optionally substituted with 1 or 2 substituents independently selected from the group W;
- R⁹ is selected from the group CN, SCN, NO₂, OH, OR¹², SR¹², S(O)R¹², S(O)₂R¹², OC(O)R¹², OS(O)₂R¹², Si(R¹²)(R¹³)(R¹⁴), C(O)OR¹², C(O)N(R¹²)R¹³, C(O)R¹², N(R¹⁰)R¹¹ and phenyl optionally substituted with 1 or 2 substituents independently selected from the group W; provided that when R⁹ is S(O)R¹², S(O)₂R¹² or OS(O)₂R¹², R¹² is other than H;

- R^{10} is selected from the group C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_1-C_5 alkoxy, C_2-C_5 alkoxyalkyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_3-C_6 haloalkynyl, C_3-C_6 cycloalkyl and C_4-C_7 cycloalkylalkyl each optionally substituted with a substituent selected from the group R^9 , $N(R^{10})R^{11}$; phenyl optionally substituted with 1 or 2 substituents independently selected from the group W; benzyl optionally substituted with 1 or 2 substituents independently selected from the group W;
- R^{11} is selected from the group H, C_1-C_6 alkyl, C_1-C_6 haloalkyl, $C(O)H$, C_2-C_3 alkylcarbonyl, C_2-C_3 alkoxy carbonyl, C_2-C_6 alkenyl and C_2-C_6 alkynyl; or
- R^{10} and R^{11} are taken together to form a member selected from the group $-CH_2CH_2CH_2CH_2CH_2-$, $-CH_2CH_2CH_2CH_2-$ and $-CH_2CH_2OCH_2CH_2-$;
- R^{12} is selected from the group H, C_1-C_3 alkyl and C_1-C_3 haloalkyl;
- R^{13} and R^{14} are independently selected from the group C_1-C_3 alkyl and C_1-C_3 haloalkyl;
- G is selected from the group $C(O)$, $C(S)$, S, $S(O)$ and $S(O)_2$;
- W is selected from the group halogen, NO_2 , CN, C_1-C_3 alkyl, C_1-C_3 haloalkyl, C_1-C_3 alkylthio, C_1-C_3 alkoxy, C_1-C_3 haloalkoxy, C_2-C_4 alkylcarbonyl and C_2-C_4 alkoxy carbonyl;
- m is 0, 1, 2, 3, 4, 5 or 6; and
- n is 0 or 1.

Preferred Compounds A are compounds wherein:

- R^1 is selected from the group CN and $C(O)OR^7$;
- R^2 is H;
- R^3 and R^4 are independently selected from the group H, halogen, CN, C_1-C_2 alkyl, C_1-C_2 haloalkyl, C_1-C_2 alkoxy and C_1-C_2 alkylthio;
- R^5 is selected from the group C_1-C_6 alkyl, C_2-C_6 alkenyl, C_1-C_6 haloalkyl, C_2-C_6 haloalkenyl and $N(R^{10})R^{11}$;
- R^9 is selected from the group CN and OR^{12} ; and
- G is selected from the group $C(O)$, S, $S(O)$ and $S(O)_2$.

- Preferred Compounds B are Compounds A wherein Q is Q-2. Preferred Compounds C are Compounds A wherein Q is Q-7. Preferred Compounds D are Compounds A wherein Q is Q-8. Preferred Compounds E are Compounds A wherein Q is Q-10. Preferred Compounds F are Compounds A wherein Q is Q-11.

Specifically preferred for biological activity is Compound G of Preferred C which is:

methyl [[[1-(propylsulfonyl)-1H-pyrazol-3-yl]oxy]sulfonyl]acetate.

- 5 Compounds of this invention can exist as one or more stereoisomers. The various stereoisomers include enantiomers, diastereomers and geometric isomers. One skilled in the art will appreciate that one stereoisomer may be more active than the others and how to separate said stereoisomers. Accordingly, the present invention comprises racemic mixtures, individual stereoisomers, and optically active mixtures of compounds of
- 10 Formula I as well as agriculturally suitable salts thereof.
- In the above recitations the term "alkyl" used either alone or in compound words such as "alkylthio" or "haloalkyl" denotes straight-chain or branched alkyl such as methyl, ethyl, *n*-propyl, *i*-propyl, or the different butyl, pentyl or hexyl isomers. "Alkenyl" denotes straight-chain or branched alkenes such as 1-propenyl, 2-propenyl,
- 15 and the different butenyl, pentenyl and hexenyl isomers. "Alkenyl" also denotes polyenes such as 1,3-butadiene and 1,3,5-hexatriene. "Alkynyl" denotes straight-chain or branched alkynes such as ethynyl, 1-propynyl, 3-propynyl and the different butynyl, pentynyl and hexynyl isomers. "Alkynyl" can also denote moieties comprised of multiple triple bonds such as 2,4-hexadiyne. "Alkoxy" denotes, for example, methoxy, ethoxy,
- 20 *n*-propyloxy, isopropyloxy and the different butoxy, pentoxy and hexyloxy isomers. "Alkenyloxy" denotes straight-chain or branched alkenyloxy moieties. Examples of alkenyloxy include $\text{H}_2\text{C}=\text{CHCH}_2\text{O}$, $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{O}$, $(\text{CH}_3)\text{CH}=\text{CHCH}_2\text{O}$, $(\text{CH}_3)\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{O}$ and $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{O}$. "Alkynyloxy" denotes straight-chain or branched alkynyloxy moieties. Examples include $\text{HC}\equiv\text{CCH}_2\text{O}$, $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{O}$ and
- 25 $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{CH}_2\text{O}$. "Alkylthio" denotes branched or straight-chain alkylthio moieties such as methylthio, ethylthio, and the different propylthio, butylthio, pentylthio and hexylthio isomers. "Alkylsulfinyl" denotes both enantiomers of an alkylsulfinyl group. For example, $\text{CH}_3\text{S}(\text{O})$, $\text{CH}_3\text{CH}_2\text{S}(\text{O})$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{S}(\text{O})$, $(\text{CH}_3)_2\text{CHS}(\text{O})$ and the different butylsulfinyl, pentylsulfinyl and hexylsulfinyl isomers. Examples of
- 30 "alkylsulfonyl" include $\text{CH}_3\text{S}(\text{O})_2$, $\text{CH}_3\text{CH}_2\text{S}(\text{O})_2$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{S}(\text{O})_2$, $(\text{CH}_3)_2\text{CHS}(\text{O})_2$ and the different butylsulfonyl, pentylsulfonyl and hexylsulfonyl isomers. "Haloalkylthio", "haloalkylsulfinyl" and "haloalkylsulfonyl" denote alkylthio, alkylsulfinyl and alkylsulfonyl substituted by halogen. "Cycloalkyl" denotes, for example, cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl. The term "cycloalkylthio" denotes
- 35 the same groups linked through an sulfur atom such as cyclopentylthio and cyclohexylthio. The term "halocycloalkylthio" denotes the cycloalkylthio substituted by halogen. "Cycloalkenyl" denotes groups such as cyclopentenyl and cyclohexenyl. The term "cycloalkylalkyl" includes cyclopropylmethyl, cyclohexylethyl, and other cycloalkyl

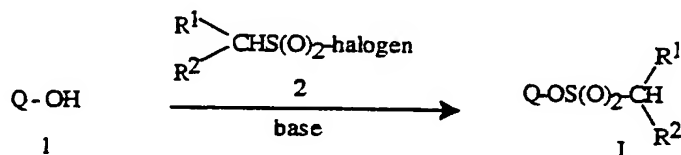
- moieties bonded to straight-chain or branched alkyl groups. The term "alkylcarbonyl" denotes carbonyl attached to an alkyl group examples include $\text{CH}_3\text{C}(\text{O})$, $\text{CH}_3\text{CH}_2\text{C}(\text{O})$ and the different propyl, butyl, pentyl and hexyl isomers. The term "alkoxycarbonyl" denotes carbonyl attached to an alkoxy group examples include $\text{CH}_3\text{OC}(\text{O})$, $\text{CH}_3\text{CH}_2\text{OC}(\text{O})$ and the different propyl, butyl, pentyl and hexyl isomers. The term "halogen", either alone or in compound words such as "haloalkyl", denotes fluorine, chlorine, bromine or iodine. Further, when used in compound words such as "haloalkyl", said alkyl may be partially or fully substituted with halogen atoms which may be the same or different. Examples of "haloalkyl" include F_3C , ClCH_2 , CF_3CH_2 and CF_3CCl_2 .
- Examples of "haloalkenyl" include $(\text{Cl})_2\text{C}=\text{CHCH}_2$ and $\text{CF}_3\text{CH}_2\text{CH}=\text{CHCH}_2$. Examples of "haloalkynyl" include $\text{HC}\equiv\text{CCHCl}$, $\text{CF}_3\text{C}\equiv\text{C}$, $\text{CCl}_3\text{C}\equiv\text{C}$ and $\text{FCH}_2\text{C}\equiv\text{CCH}_2$. Examples of "haloalkoxy" include CF_3O , $\text{CCl}_3\text{CH}_2\text{O}$, $\text{CF}_2\text{HCH}_2\text{CH}_2\text{O}$ and $\text{CF}_3\text{CH}_2\text{O}$. Examples of "haloalkylthio" include CCl_3S , CF_3S , $\text{CCl}_3\text{CH}_2\text{S}$ and $\text{CH}_2\text{ClCH}_2\text{CH}_2\text{S}$. Examples of "haloalkylsulfonyl" include $\text{CF}_3\text{S}(\text{O})_2$, $\text{CCl}_3\text{S}(\text{O})_2$, $\text{CF}_3\text{CH}_2\text{S}(\text{O})_2$ and $\text{CF}_3\text{CF}_2\text{S}(\text{O})_2$. The total number of carbon atoms in a substituent group is indicated by the " $\text{C}_i\text{-C}_j$ " prefix where i and j are numbers from 1 to 7. For example, $\text{C}_1\text{-C}_3$ alkylsulfonyl designates methylsulfonyl through propylsulfonyl.

- When a compound is substituted with a substituent bearing a subscript that indicates the number of said substituents can exceed 1, said substituents (when they exceed 1) are independently selected from the group of defined substituents.

DETAILS OF THE INVENTION

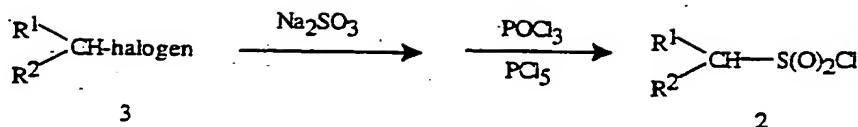
- Compounds of Formula I can be prepared by reaction of the corresponding hydroxy compound (1) with the appropriate sulfonyl halide (2) and a base such as triethylamine or pyridine in a solvent such as dichloromethane or tetrahydrofuran as shown in Equation 1.
- In Equations 1-11, R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and G are as previously defined.

Equation 1



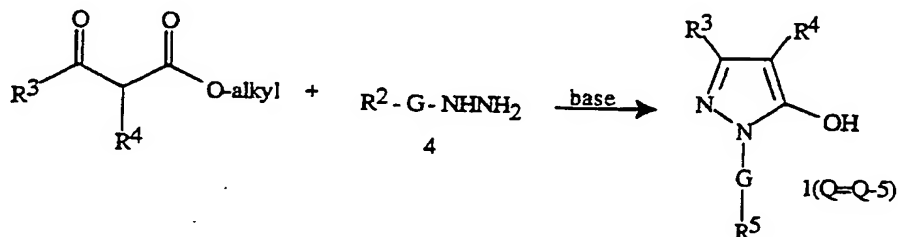
- Sulfonyl halides 2 can be prepared by the reaction of an alkyl halide (3) with sodium sulfite followed by reaction with a halogenating agent such as phosphorous oxychloride and/or phosphorous pentachloride as shown in Equation 2. Sulfonyl halides can be also be prepared by other methods known to one skilled in the art (see Hoyle, J., *In the Chemistry of Sulphonic Acids, Esters and their Derivatives*; Patai, S. and Rappoport, Z., Eds.; Wiley: New York, (1991), pp 351-399).

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Equation 2

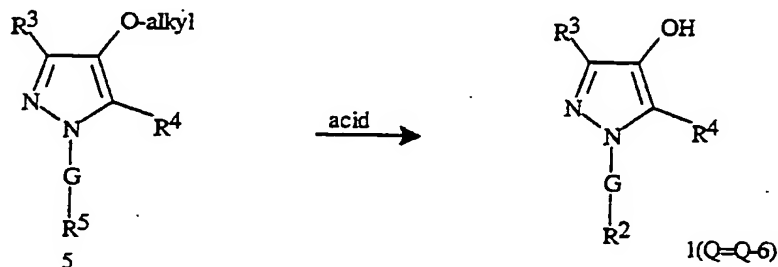
It is known that Compounds 1 can exist as the carbonyl tautomer depending on the nature of the Q group. The synthesis of hydroxy Compounds 1 wherein Q is Q-1, Q-2, Q-3, Q-4, Q-8, Q-9 or Q-10 is described in the art.

A general review for the synthesis of hydroxypyrazoles can be found in Wiley, et al., *The Chemistry of Heterocyclic Compounds, Pyrazolones, Pyrazolidones and Derivatives*, Vol. 20, Wiley, New York, (1964). More specifically, the hydroxy Compounds 1 wherein Q is Q-5 can be prepared from the appropriate β -dicarbonyl compound or a synthetic equivalent such as acetylenic ester or α -oxodithioetene acetal and the appropriate Compound 4 in the presence of base as shown in Equation 3. The synthesis of Compounds 4 is known.

Equation 3

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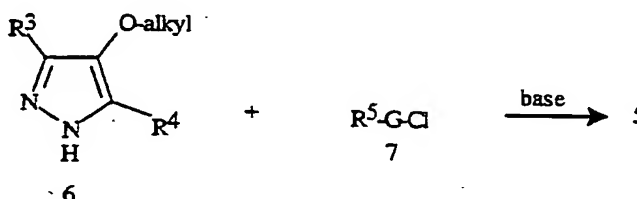
Hydroxy Compounds 1 wherein Q is Q-6 can be prepared from alkoxy compounds 5 by treatment with iodotrimethylsilane or aqueous acid such as hydrobromic acid in acetic acid as shown in Equation 4.

Equation 4

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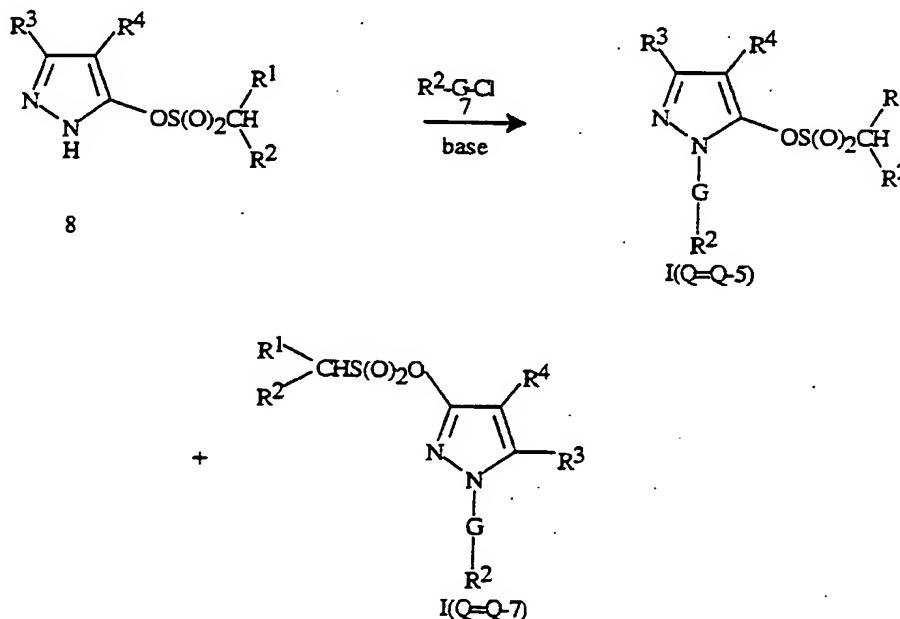
The compounds of Formula 5 can be prepared by treatment of an alkoxy pyrazole 6 with the appropriate reagent (7) and base as shown in Equation 5. The synthesis of 4-alkoxy pyrazoles is known to one skilled in the art see, for example, Pluempe, H. and Schegk, E., *Arch. Pharm.*, 300, 704, (1967).

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Equation 5

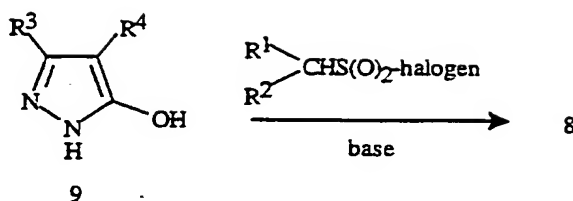
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Alternatively, compounds of Formula I wherein Q is Q-5 or Q-7 can be prepared by reaction of a pyrazole sulfonate 8 with a compound of Formula 7 and base as shown in Equation 6. The ratio of products obtained will depend on the nature of the R³ and R⁴ groups. In some instances, only one product will be obtained.

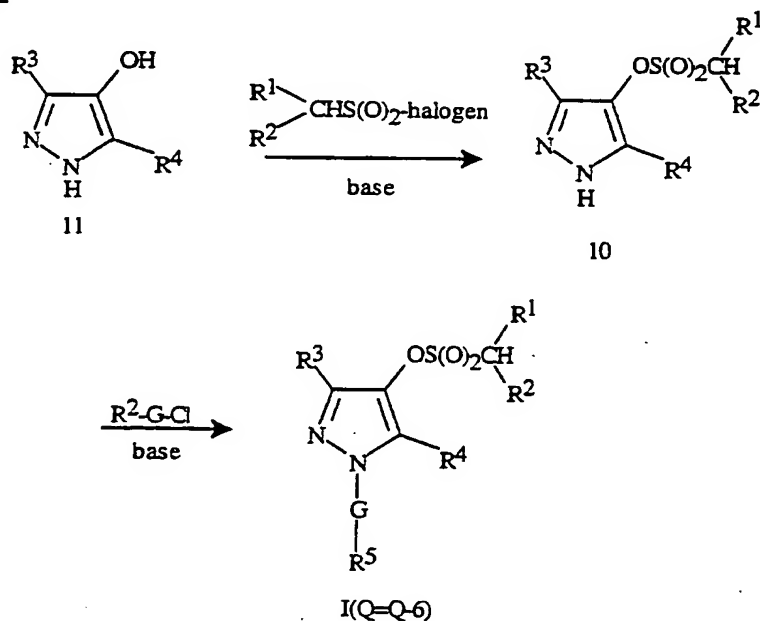
Equation 6

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The compounds of Formula 8 can be prepared by the reaction of a hydroxypyrazole 9 with a sulfonyl halide and base as shown in Equation 7. The synthesis of compounds of Formula 9 is known.

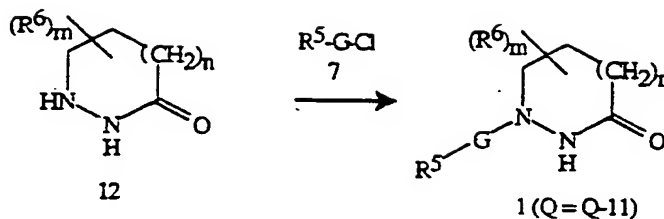
Equation 7

5 Analogously, compounds of Formula I wherein Q is Q-6 can be prepared from pyrazole sulfonates of Formula 10 which in turn can be prepared from hydroxy pyrazoles of Formula 11 as shown in Equation 8.

Equation 8

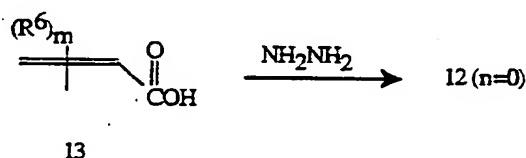
10 The hydroxy Compounds 1 wherein Q is Q-11 (which will exist predominantly as the carbonyl tautomer) can be prepared by treatment of the NH heterocycle 12 with the appropriate reagent 7 as shown in Equation 9.

10

Equation 9

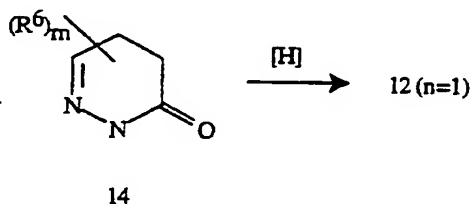
The compounds of Formula 12 wherein $n=0$ can be prepared from the appropriate α , β unsaturated acid (or ester) 13 and hydrazine as shown in Equation 10.

5

Equation 10

The compounds of Formula 12 wherein $n=1$ can be prepared by reduction of the corresponding compound of Formula 14 as shown in Equation 11. The synthesis of compounds of Formula 14 is known to one skilled in the art.

10

Equation 11

It is recognized that some reagents and reaction conditions described above for preparing compounds of Formula I may not be compatible with certain functionalities present in the intermediates. In these instances, the incorporation of protection/deprotection sequences into the synthesis will aid in obtaining the desired products. The use and choice of the protecting group will be apparent to one skilled in chemical synthesis.

15

EXAMPLE 1Preparation of Methyl [1-((1-(Propylsulfonyl)-
1H-pyrazol-3-yl)oxy)sulfonyl]acetateIntermediate 15 Methyl-[[1-(1H-pyrazol-3-yl)oxy]sulfonyl]acetate

To a solution of 3 g (36 mmol) of 2,4-dihydro-3H-pyrazol-3-one in 180 mL of tetrahydrofuran at 0°C was added 6.0 mL (43 mmol) of triethylamine followed by the slow addition of 4.9 mL (43 mmol) of methyl (chlorosulfonyl) acetate. The reaction mixture was stirred overnight at room temperature. The solvent was removed with a rotary evaporator. The residue was dissolved in dichloromethane, washed with water and dried (Na₂SO₄). The solvent was removed with a rotary evaporator. The residue was purified by flash chromatography (35-50% ethyl acetate in hexanes as eluant) to afford 1.97 g of the title compound as a colorless oil. ¹H NMR (CDCl₃): δ 3.86 (s,3), 4.91 (s,2), 6.23 (s,1), 7.54 (s,1).

15 Methyl [1-((1-(Propylsulfonyl)-1H-pyrazol-
3-yl)oxy)sulfonyl]acetate

To a solution of 1.97 g (8.9 mmol) of methyl [[1-(1H-pyrazol-3-yl)oxy]sulfonyl]acetate in 45 mL of dichloromethane at 0°C was added 1.75 mL (12.5 mmol) of triethylamine and 1.41 mL (12.5 mmol) of propanesulfonyl chloride. The reaction mixture was stirred overnight at room temperature. The reaction mixture was then cooled to 0°C and 0.62 mL (4.4 mmol) of triethylamine and 0.51 mL (4.4 mmol) of propanesulfonyl chloride were added. The reaction mixture was stirred overnight at room temperature. It was washed with water and dried (Na₂SO₄). The solvent was removed with a rotary evaporator. The residue was purified by flash chromatography (30-50% ethyl acetate in hexanes as eluant) to afford 0.47 g of the title compound as a colorless oil. ¹H NMR (CDCl₃): δ 1.04 (t,3), 1.75 (m,2), 3.44 (m,2), 3.87 (s,3), 6.38 (s,1), 8.00 (s,1).

By applying the procedures of Example 1 and Equations 1 through 11, one skilled in the art can prepare the compounds in Tables 1 through 4. In the following Tables, abbreviations for G, various alkyl chains and rings have been used with the following corresponding definitions.

- Me = methyl = CH₃
 Et = ethyl = CH₂CH₃
 iPr = isopropyl = CH(CH₃)₂
 nPr = n-propyl = CH₂CH₂CH₃
 cPr = cyclopropyl = CH(CH₃)₂
 iBu = isobutyl = CH₂CH(CH₃)₂
 sBu = s-butyl = CH(CH₃)CH₂CH₃

tBu = *tert*-butyl = C(CH₃)₃

nBu = *n*-butyl = (CH₂)₃CH₃

iAm = isoamyl = CH₂CH₂CH(CH₃)₂

Ph = phenyl = C₆H₅

5 cPrCH₃ = 2-cyclopropylmethyl = CH(CH₂CH₂)CH₂

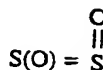
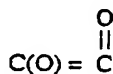
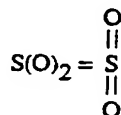
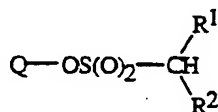


Table 1



10

R¹=C(O)OCH₃, R²=H, R³=H

Q	G	R ⁵
Q-1	S	iBu
Q-1	S(O)	CH ₂ CH=CH ₂
15 Q-1	S(O) ₂	N(H)iPr
Q-1	C(O)	N(H)sBu
Q-3	S	iBu
Q-3	C(O)	N(H)sBu
Q-3	C(O)	N(CH ₃)CH ₂ CN
20 Q-3	S(O) ₂	nPr
Q-4	S	iBu
Q-4	C(O)	N(H)sBu
Q-4	C(O)	N(H)iPr
Q-4	S(O) ₂	nPr
25 R ¹ =C(O)OCH ₃ , R ² =H, R ³ =H, R ⁴ =H		
Q	G	R ⁵
Q-5	C(O)	N(H)sBu
Q-5	C(O)	N(H)iPr
Q-5	S(O) ₂	nPr
30 Q-6	C(O)	N(H)sBu
Q-6	C(O)	N(H)iPr
Q-6	C(O)	nPr

R¹=C(O)OEt, R²=H, R³=CH₃, R⁴=H

35 Q	G	R ⁵
Q-5	C(O)	N(H)sBu
Q-5	S(O) ₂	iBu
Q-5	S(O) ₂	nPr
Q-6	C(O)	N(H)sBu
40 Q-6	S(O) ₂	iBu
Q-6	S(O) ₂	nPr

R¹=C(O)OCH₃, R²=H, R³=CH₃

Q	G	R ⁵
45 Q-8	C(O)	N(H)iPr
Q-8	S(O) ₂	nPr
Q-8	S(O) ₂	iBu
Q-8	C(O)	N(H)sBu
Q-9	C(O)	N(H)iPr
50 Q-9	S(O) ₂	nPr
Q-9	S(O) ₂	iBu
Q-9	C(O)	N(H)sBu

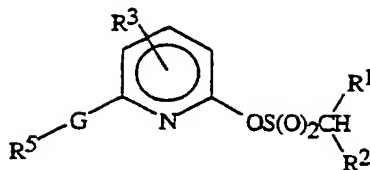
R¹=C(O)OEt, R²=H, R³=Ph

55 Q	G	R ⁵
Q-8	C(O)	N(H)cPr

Q-8	S(O) ₂	nPr
Q-8	S(O) ₂	iBu
Q-9	C(O)	N(H)cPr

Q-9	S(O) ₂	nPr
5 Q-9	S(O) ₂	iBu

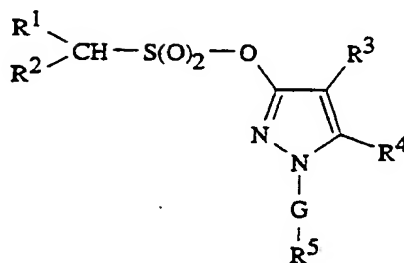
Table 2



G=S(O) ₂ ,	G=S,	G=C(O),	G=S(O),
R ¹ =C(O)OCH ₃ ,	R ¹ =C(O)OCH ₃ ,	R ¹ =C(O)OCH ₃ ,	R ¹ =C(O)OCH ₃ ,
R ² =H, R ³ =H,	R ² =H, R ³ =H,	R ² =H, R ³ =H,	R ² =H, R ³ =H,
<u>R⁵</u> =	<u>R⁵</u> =	<u>R⁵</u> =	<u>R⁵</u> =
CH ₃	CH ₃	CH ₃	CH ₃
C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅
nPr	nPr	nPr	nPr
iPr	iPr	iPr	iPr
cPr	cPr	cPr	cPr
nBu	nBu	nBu	nBu
iBu	iBu	iBu	iBu
tBu	tBu	tBu	tBu
sBu	sBu	sBu	sBu
iAm	iAm	iAm	iAm
CH ₂ CH=CH ₂	CH ₂ CH=CH ₂	CH ₂ CH=CH ₂	CH ₂ CH=CH ₂
CH ₂ C≡CH	CH ₂ C≡CH	CH ₂ C≡CH	CH ₂ C≡CH
CH ₂ CH ₂ CH ₂ Cl	CH ₂ CH ₂ CH ₂ Cl	CH ₂ CH ₂ CH ₂ Cl	CH ₂ CH ₂ CH ₂ Cl
CH ₂ CH ₂ C(F)=CF ₂	CH ₂ CH ₂ C(F)=CF ₂	CH ₂ CH ₂ C(F)=CF ₂	CH ₂ CH ₂ C(F)=CF ₂
CH ₂ cPr	CH ₂ cPr	CH ₂ cPr	CH ₂ cPr
N(H)iPr	N(H)iPr	N(H)iPr	N(H)iPr
N(H)sBu	N(H)sBu	N(H)sBu	N(H)sBu

G=S(O) ₂ , R ³ =H, R ⁵ =iBu		G=C(O), R ³ =H, R ⁵ =N(H)sBu	
<u>R¹</u>	<u>R²</u>	<u>R¹</u>	<u>R²</u>
CN	H	CN	H
NO ₂	H	NO ₂	H
OCH ₃	H	OCH ₃	H
C(O)OiPr	H	C(O)OiPr	H
C(O)N(CH ₃) ₂	H	C(O)N(CH ₃) ₂	H
SCH ₃	H	SCH ₃	H
S(O) ₂ N(CH ₃) ₂	H	S(O) ₂ N(CH ₃) ₂	H
C(O)OCH ₃	CH ₃	C(O)OCH ₃	CH ₃
C(O)OCH ₃	CN	C(O)OCH ₃	CN
C(O)OCH ₃	C(O)OCH ₃	C(O)OCH ₃	C(O)OCH ₃
C(O)OCH ₃	C(O)N(CH ₃) ₂	C(O)OCH ₃	C(O)N(CH ₃) ₂

Table 3

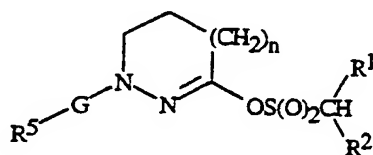


G=S(O) ₂ , R ² =H, R ¹ =C(O)OCH ₃ , R ³ =H, R ⁴ =CH ₃ , <u>R⁵</u> =	G=S(O) ₂ , R ² =H, R ¹ =C(O)OCH ₃ , R ³ =H, R ⁴ =H, <u>R⁵</u> =	G=C(O), R ² =H, R ¹ =C(O)OCH ₃ , R ³ =H, R ⁴ =CH ₃ , <u>R⁵</u> =	G=C(O), R ² =H, R ¹ =C(O)OCH ₃ , R ³ =H, R ⁴ =H, <u>R⁵</u> =
CH ₃	CH ₃	CH ₃	CH ₃
C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅
nPr	nPr	nPr	nPr
iPr	iPr	iPr	iPr
cPr	cPr	cPr	cPr
nBu	nBu	nBu	nBu
iBu	iBu	iBu	iBu
tBu	tBu	tBu	tBu
sBu	sBu	sBu	sBu
iAm	iAm	iAm	iAm

CH ₂ CH=CH ₂	CH ₂ CH=CH ₂	CH ₂ CH=CH ₂	CH ₂ CH=CH ₂
CH ₂ C≡CH	CH ₂ C≡CH	CH ₂ C≡CH	CH ₂ C≡CH
CH ₂ CH ₂ CH ₂ Cl	CH ₂ CH ₂ CH ₂ Cl	CH ₂ CH ₂ CH ₂ Cl	CH ₂ CH ₂ CH ₂ Cl
CH ₂ CH ₂ C(F)=CF ₂	CH ₂ CH ₂ C(F)=CF ₂	CH ₂ CH ₂ C(F)=CF ₂	CH ₂ CH ₂ C(F)=CF ₂
CH ₂ cPr	CH ₂ cPr	CH ₂ cPr	CH ₂ cPr
N(H)iPr	N(H)iPr	N(H)iPr	N(H)iPr
N(H)sBu	N(H)sBu	N(H)sBu	N(H)sBu
CH ₂ SCH ₃	CH ₂ SCH ₃	N(CH ₃)iPr	N(CH ₃)iPr
CH ₂ Si(CH ₃) ₃	CH ₂ Si(CH ₃) ₃	N(H)cPr	N(H)cPr
CH ₂ CN	CH ₂ CN	N(CH ₃)C ₂ H ₅	N(CH ₃)C ₂ H ₅
CH ₂ S(O) ₂ CH ₃	CH ₂ S(O) ₂ CH ₃	N(H)CH(CH ₃)CH ₂ CN	N(H)CH(CH ₃)CH ₂ CN

G=S(O) ₂ , R ³ =H, R ⁴ =H, R ⁵ =Pr		G=C(O), R ³ =H, R ⁴ =H, R ⁵ =sBu	
R ¹	R ²	R ¹	R ²
CN	H	CN	H
NO ₂	H	NO ₂	H
OCH ₃	H	OCH ₃	H
C(O)OiPr	H	C(O)OiPr	H
C(O)N(CH ₃) ₂	H	C(O)N(CH ₃) ₂	H
SCH ₃	H	SCH ₃	H
S(O) ₂ N(CH ₃) ₂	H	S(O) ₂ N(CH ₃) ₂	H
C(O)OCH ₃	CH ₃	C(O)OCH ₃	CH ₃
C(O)OCH ₃	CN	C(O)OCH ₃	CN
C(O)OCH ₃	C(O)OCH ₃	C(O)OCH ₃	C(O)OCH ₃
C(O)OCH ₃	C(O)N(CH ₃) ₂	C(O)OCH ₃	C(O)N(CH ₃) ₂

Table 4



$G=S(O)_2, n=0,$ $R^1=C(O)OCH_3,$ $R^2=H,$ $\underline{R^5}=$	$G=S(O)_2, n=1$ $R^1=C(O)CH_3,$ $R^2=H,$ $\underline{R^5}=$	$G=C(O), n=0$ $R^1=C(O)OCH_3,$ $R^2=H,$ $\underline{R^5}=$	$G=C(O), n=1$ $R^1=C(O)OCH_3,$ $R^2=H,$ $\underline{R^5}=$
CH ₃	CH ₃	CH ₃	CH ₃
C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅
nPr	nPr	nPr	nPr
iPr	iPr	iPr	iPr
cPr	cPr	cPr	cPr
nBu	nBu	nBu	nBu
iBu	iBu	iBu	iBu
tBu	tBu	tBu	tBu
sBu	sBu	sBu	sBu
iAm	iAm	iAm	iAm
CH ₂ CH=CH ₂	CH ₂ CH=CH ₂	CH ₂ CH=CH ₂	CH ₂ CH=CH ₂
CH ₂ C≡CH	CH ₂ C≡CH	CH ₂ C≡CH	CH ₂ C≡CH
CH ₂ CH ₂ CH ₂ Cl	CH ₂ CH ₂ CH ₂ Cl	CH ₂ CH ₂ CH ₂ Cl	CH ₂ CH ₂ CH ₂ Cl
CH ₂ CH ₂ C(F)=CF ₂	CH ₂ CH ₂ C(F)=CF ₂	CH ₂ CH ₂ C(F)=CF ₂	CH ₂ CH ₂ C(F)=CF ₂
CH ₂ cPr	CH ₂ cPr	CH ₂ cPr	CH ₂ cPr
N(H)iPr	N(H)iPr	N(H)iPr	N(H)iPr
N(H)sBu	N(H)sBu	N(H)sBu	N(H)sBu

 $G=S(O)_2, n=0, R^5=Pr$

R^1	R^2
CN	H
NO ₂	H
OCH ₃	H
C(O)OiPr	H
C(O)N(CH ₃) ₂	H
SCH ₃	H
S(O) ₂ N(CH ₃) ₂	H
C(O)OCH ₃	CH ₃
C(O)OCH ₃	CN
C(O)OCH ₃	C(O)OCH ₃
C(O)OCH ₃	C(O)N(CH ₃) ₂

 $G=C(O), n=1, R^5=N(H)sBu$

R^1	R^2
CN	H
NO ₂	H
OCH ₃	H
C(O)OiPr	H
C(O)N(CH ₃) ₂	H
SCH ₃	H
S(O) ₂ N(CH ₃) ₂	H
C(O)OCH ₃	CH ₃
C(O)OCH ₃	CN
C(O)OCH ₃	C(O)OCH ₃
C(O)OCH ₃	C(O)N(CH ₃) ₂

Formulation/Utility

Compounds of this invention will generally be used in formulation with an agriculturally suitable carrier comprising a liquid or solid diluent. Useful formulations include dusts, granules, baits, pellets, solutions, suspensions, emulsions, wettable powders, emulsifiable concentrates, dry flowables and the like, consistent with the physical properties of the active ingredient, mode of application and environmental factors such as soil type, moisture and temperature. Sprayable formulations can be extended in suitable media and used at spray volumes from about one to several hundred liters per hectare. High strength compositions are primarily used as intermediates for further formulation. The formulations will typically contain effective amounts of active ingredient, diluent and surfactant within the following approximate ranges which add up 100 weight percent.

	Weight Percent		
	<u>Active Ingredient</u>	<u>Diluent</u>	<u>Surfactant</u>
Wettable Powders	5-90	0-74	1-10
Oil Suspensions, Emulsions, Solutions, (including Emulsifiable Concentrates)	5-50	40-95	0-15
Dusts	1-25	70-99	0-5
Granules, Baits and Pellets	0.01-99	5-99.99	0-15
High Strength Compositions	90-99	0-10	0-2

Typical solid diluents are described in Watkins, et al., *Handbook of Insecticide Dust Diluents and Carriers*, 2nd Ed., Dorland Books, Caldwell, New Jersey. Typical liquid diluents and solvents are described in Marsden, *Solvents Guide*, 2nd Ed., Interscience, New York, 1950. *McCutcheon's Detergents and Emulsifiers Annual*, Allured Publ. Corp., Ridgewood, New Jersey, as well as Sisely and Wood, *Encyclopedia of Surface Active Agents*, Chemical Publ. Co., Inc., New York, 1964, list surfactants and recommended uses. All formulations can contain minor amounts of additives to reduce foam, caking, corrosion, microbiological growth, and the like.

Solutions are prepared by simply mixing the ingredients. Fine solid compositions are made by blending and, usually, grinding as in a hammer mill or fluid energy mill. Water-dispersible granules can be produced by agglomerating a fine powder composition; see for example, Cross et al., *Pesticide Formulations*, Washington, D.C., 1988, pp 251-259. Suspensions are prepared by wet-milling; see, for example, U.S. 3,060,084. Granules and pellets can be made by spraying the active material upon preformed granular carriers or by agglomeration techniques. See Browning,

"Agglomeration", *Chemical Engineering*, December 4, 1967, pp 147-148, *Perry's Chemical Engineer's Handbook*, 4th Ed., McGraw-Hill, New York, 1963, pages 8-57 and following, and WO 91/13546.

- For further information regarding the art of formulation, see U.S. 3,235,361, Col. 6, line 16 through Col. 7, line 19 and Examples 10-41; U.S. 3,309,192, Col. 5, line 43 through Col. 7, line 62 and Examples 8, 12, 15, 39, 41, 52, 53, 58, 132, 138-140, 162-164, 166, 167 and 169-182; U.S. 2,891,855, Col. 3, line 66 through Col. 5, line 17 and Examples 1-4; Klingman, *Weed Control as a Science*, John Wiley and Sons, Inc., New York, 1961, pp 81-96; and Hance et al., *Weed Control Handbook*, 8th Ed., Blackwell Scientific Publications, Oxford, 1989.

In the following Examples, all percentages are by weight and all formulations are prepared in conventional ways. Compound numbers refer to compounds in Index Table A.

Example A

15 Wettable Powder

Compound 1	65.0%
dodecylphenol polyethylene glycol ether	2.0%
sodium ligninsulfonate	4.0%
sodium silicoaluminate	6.0%
20 montmorillonite (calcined)	23.0%.

Example B

Granule

Compound 1	10.0%
attapulgate granules (low volatile matter, 0.71/0.30 mm; U.S.S. No. 25-50 sieves)	90.0%.

Example C

Extruded Pellet

Compound 1	25.0%
30 anhydrous sodium sulfate	10.0%
crude calcium ligninsulfonate	5.0%
sodium alkyl naphthalenesulfonate	1.0%
calcium/magnesium bentonite	59.0%.

Example D

35 Emulsifiable Concentrate

Compound 1	20.0%
blend of oil soluble sulfonates	

and polyoxyethylene ethers	10.0%
isophorone	70.0%.

The compounds of this invention exhibit activity against a wide spectrum of foliar-feeding, fruit-feeding, stem or root feeding, seed-feeding, aquatic and soil-inhabiting arthropods (term "arthropods" includes insects, mites and nematodes) which are pests of growing and stored agronomic crops, forestry, greenhouse crops, ornamentals, nursery crops, stored food and fiber products, livestock, household, and public and animal health. Those skilled in the art will appreciate that not all compounds are equally effective against all growth stages of all pests. Nevertheless, all of the compounds of this invention display activity against pests that include: eggs, larvae and adults of the Order Lepidoptera; eggs, foliar-feeding, fruit-feeding, root-feeding, seed-feeding larvae and adults of the Order Coleoptera; eggs, immatures and adults of the Orders Hemiptera and Homoptera; eggs, larvae, nymphs and adults of the Order Acari; eggs, immatures and adults of the Orders Thysanoptera, Orthoptera and Dermaptera; eggs, immatures and adults of the Order Diptera; and eggs, juveniles and adults of the Phylum Nematoda. The compounds of this invention are also active against pests of the Orders Hymenoptera, Isoptera, Siphonaptera, Blattaria, Thysanura and Psocoptera; pests belonging to the Class Arachnida and Phylum Platyhelminthes. Specifically, the compounds are active against southern corn rootworm (*Diabrotica undecimpunctata howardi*), aster leafhopper (*Mascrostes fascifrons*), boll weevil (*Anthonomus grandis*), two-spotted spider mite (*Tetranychus urticae*), fall armyworm (*Spodoptera frugiperda*), black bean aphid (*Aphis fabae*), green peach aphid (*Myzus persica*), cotton aphid (*Aphis gossypii*), Russian wheat aphid (*Diuraphis noxia*), English grain aphid (*Sitobion avenae*), tobacco budworm (*Heliothis virescens*), rice water weevil (*Lissorhoptrus oryzophilus*), rice leaf beetle (*Oulema oryzae*), whitebacked planthopper (*Sogatella furcifera*), green leafhopper (*Nephotettix cincticeps*), brown planthopper (*Nilaparvata lugens*), small brown planthopper (*Laodelphax striatellus*), rice stem borer (*Chilo suppressalis*), rice leafroller (*Cnaphalocrocis medinalis*), black rice stink bug (*Scotinophara lurida*), rice stink bug (*Oebalus pugnax*), rice bug (*Leptocoris chinensis*), slender rice bug (*Cletus punctiger*), and southern green stink bug (*Nezara viridula*). The compounds are active on mites, demonstrating ovicidal, larvicidal and chemosterilant activity against such families as Tetranychidae including *Tetranychus urticae*, *Tetranychus cinnabarinus*, *Tetranychus mcdanieli*, *Tetranychus pacificus*, *Tetranychus turkestanii*, *Byrobia rubrioculus*, *Panonychus ulmi*, *Panonychus citri*, *Eotetranychus carpini borealis*, *Eotetranychus*, *hicoriae*, *Eotetranychus sexmaculatus*, *Eotetranychus yumensis*, *Eotetranychus banksi* and *Oligonychus pratensis*; Tenuipalpidae including *Brevipalpus lewisi*, *Brevipalpus phoenicis*, *Brevipalpus californicus* and *Brevipalpus obovatus*; Eriophyidae including *Phyllocoptruta oleivora*,

Eriophyes sheldoni, *Aculus cornutus*, *Epirimerus pyri* and *Eriophyes mangiferae*. See WO 90/10623 and WO 92/00673 for more detailed pest descriptions.

Compounds of this invention can also be mixed with one or more other insecticides, fungicides, nematocides, bactericides, acaricides, growth regulators, chemosterilants, semiochemicals, repellants, attractants, pheromones, feeding stimulants or other biologically active compounds to form a multi-component pesticide giving an even broader spectrum of agricultural protection. Examples of other agricultural protectants with which compounds of this invention can be formulated are: insecticides such as avermectin B, monocrotophos, carbofuran, tetrachlorvinphos, malathion, parathion-methyl, methomyl, chlordimeform, diazinon, deltamethrin, oxamyl, fenvalerate, esfenvalerate, permethrin, profenofos, sulprofos, triflumuron, diflubenzuron, methoprene, buprofezin, thiodicarb, acephate, azinphosmethyl, chlorpyrifos, dimethoate, fipronil, flufenprox, fonophos, isofenphos, methidathion, metha-midophos, phosmet, phosphamidon, phosalone, pirimicarb, phorate, terbufos, trichlorfon, methoxychlor, bifenthrin, biphenate, cyfluthrin, tefluthrin, fenpropathrin, fluvalinate, flucythrinate, tralomethrin, imidacloprid, metaldehyde and rotenone; fungicides such as carbendazim, thiuram, dodine, maneb, chloroneb, benomyl, cymoxanil, fenpropidine, fenpropimorph, triadimefon, captan, thiophanate-methyl, thiabendazole, phosethyl-Al, chlorothalonil, dichloran, metalaxyl, captafol, iprodione, oxadixyl, vinclozolin, kasugamycin, myclobutanil, tebuconazole, difenoconazole, diniconazole, fluquinconazole, ipconazole, metconazole, penconazole, propiconazole, uniconazole, flutriafol, prochloraz, pyrifeno, fenarimol, triadimenol, diclobutrazol, copper oxychloride, furalaxyl, folpet, flusilazol, blasticidin S, diclomezine, edifenphos, isoprothiolane, iprobenfos, mepronil, neo-asozin, pencycuron, probenazole, pyroquilon, tricyclazole, validamycin, and flutolanil; nematocides such as aldoxycarb, fenamiphos and fosthietan; bactericides such as oxytetracycline, streptomycin and tribasic copper sulfate; acaricides such as binapacryl, oxythioquinox, chlorobenzilate, dicofol, dienochlor, cyhexatin, hexythiazox, amitraz, propargite, tebufenpyrad and fenbutatin oxide; and biological agents such as entomopathogenic bacteria, virus and fungi.

In certain instances, combinations with other arthropodicides having a similar spectrum of control but a different mode of action will be particularly advantageous for resistance management.

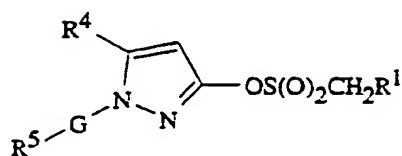
Arthropod pests are controlled and protection of agronomic, horticultural and specialty crops, animal and human health is achieved by applying one or more of the compounds of this invention, in an effective amount, to the environment of the pests including the agronomic and/or nonagronomic locus of infestation, to the area to be protected, or directly on the pests to be controlled. Thus, the present invention further comprises a method for the control of foliar and soil inhabiting arthropods and nematode

pests and protection of agronomic and/or nonagronomic crops, comprising applying one or more of the compounds of Formula I, or compositions containing at least one such compound, in an effective amount, to the environment of the pests including the agronomic and/or nonagronomic locus of infestation, to the area to be protected, or
5 directly on the pests to be controlled. A preferred method of application is by spraying. Alternatively, granular formulations of these compounds can be applied to the plant foliage or the soil. Other methods of application include direct and residual sprays, aerial sprays, seed coats, microencapsulations, systemic uptake, baits, eartags, boluses, foggers, fumigants, aerosols, dusts and many others. The compounds can be
10 incorporated into baits that are consumed by the arthropods or in devices such as traps and the like.

The compounds of this invention can be applied in their pure state, but most often application will be of a formulation comprising one or more compounds with suitable carriers, diluents, and surfactants and possibly in combination with a food depending on
15 the contemplated end use. A preferred method of application involves spraying a water dispersion or refined oil solution of the compounds. Combinations with spray oils, spray oil concentrations, spreader stickers, adjuvants, and synergists and other solvents such as piperonyl butoxide often enhance compound efficacy.

The rate of application required for effective control will depend on such factors as
20 the species of arthropod to be controlled, the pest's life cycle, life stage, its size, location, time of year, host crop or animal, feeding behavior, mating behavior, ambient moisture, temperature, and the like. Under normal circumstances, application rates of about 0.01 to 2 kg of active ingredient per hectare are sufficient to control pests in agronomic ecosystems, but as little as 0.001 kg/hectare may be sufficient or as much as 8 kg hectare
25 may be required. For nonagronomic applications, effective use rates will range from about 1.0 to 50 mg/square meter but as little as 0.1 mg/square meter may be sufficient or as much as 150 mg/square meter may be required.

The following TESTS demonstrate the control efficacy of compounds of this invention on specific pests. "Control efficacy" represents inhibition of arthropod
30 development (including mortality) that causes significantly reduced feeding. The pest control protection afforded by the compounds is not limited, however, to these species. See Index Tables A-E for compound descriptions.

Index Table A

<u>Compound</u>	<u>G</u>	<u>R¹</u>	<u>R⁴</u>	<u>R⁵</u>	<u>m.p. (°C)</u>
1	S(O) ₂	C(O)OCH ₃	CH ₃	nPr	oil ^a
2	S(O) ₂	CN	CH ₃	nPr	oil ^b
3	S(O) ₂	CN	H	nPr	oil ^c
4	S(O) ₂	C(O)OCH ₃	H	nPr	oil ^d
5	S(O) ₂	C(O)OC ₂ H ₅	CH ₃	nPr	oil ^e

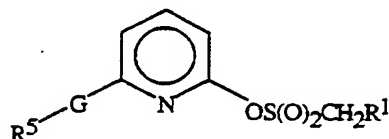
a ¹H NMR (CDCl₃) δ 1.04 (t,3H), 1.75 (m,2H), 2.54 (s,3H) 3.42 (m,2H), 3.86 (s,3H), 4.52 (s,2H), 6.08 (s,1H).

b ¹H NMR (CDCl₃) δ 1.05 (t,3H), 1.75 (m,2H), 2.57 (s,3H), 3.44 (m,2H), 4.58 (s,2H), 6.10 (s,1H).

c ¹H NMR (CDCl₃) δ 1.05 (t,3H), 1.75 (m,2H), 3.47 (m,2H), 4.59 (s,2H), 6.40 (s,1H), 8.04 (s,1H).

d ¹H NMR reported in Example 1.

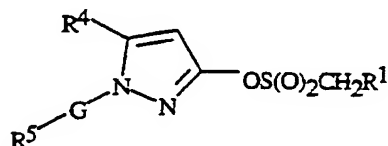
e ¹H NMR (CDCl₃) δ 1.05 (t,3H), 1.31 (t,3H), 1.75 (m,2H), 2.55 (s,3H), (s,3H), 3.44 (m,2H), 4.31 (q,2H), 4.49 (s,2H), 6.09 (s,1H).

Index Table B

<u>Compound</u>	<u>G</u>	<u>R¹</u>	<u>R⁵</u>	<u>m.p. (°C)</u>
6	S	C(O)OCH ₃	iBu	oil ^f
7	S(O) ₂	C(O)OCH ₃	iBu	oil ^g
8	S(O)	C(O)OCH ₃	iBu	oil ^h
9	S	S(O) ₂ CH ₃	iBu	79-81
10	C(O)	C(O)OCH ₃	N(H)sBu	oil ⁱ
11	C(O)	C(O)OCH ₃	N(H)iPr	94-95
12	S	CN	CH ₂ Ph	oil ^j

f ¹H NMR (CDCl₃) δ 1.04 (d,6H), 1.98 (m,1H), 3.01 (d,2H), 3.87 (s,3H), 4.71 (s,2H), 6.77 (d,1H), 7.15 (d,1H), 7.57 (dd,1H).

- g ^1H NMR (CDCl_3) δ 1.05 (d,6H), 2.22 (m,1H), 3.26 (d,2H), 3.86 (s,3H), 4.75 (s,2H), 7.38 (d,1H), 8.09 (m,2H).
- h ^1H NMR (CDCl_3) δ 1.07 (d,3H), 1.20 (d,3H), 2.37 (m,1H), 2.85 (m,2H), 3.87 (s,3H), 4.65 (m,2H), 7.20 (d,1H), 8.01 (d,1H), 8.09 (dd,1H).
- 5 i ^1H NMR (CDCl_3) δ 0.97 (t,3H), 1.27 (d,3H), 1.62 (m,2H), 3.89 (s,3H), 4.15 (m,1H), 4.53 (s,2H), 7.30 (d,1H), 8.65 (br,1H), 8.02 (dd,1H), 8.23 (d,1H).
- j ^1H NMR (CDCl_3) δ 4.2 (s,2H), 4.4 (s,2H), 6.8-7.8 (m,8H).

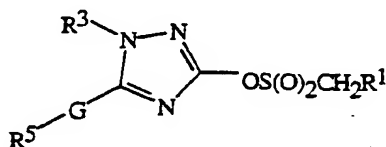
Index Table C

10

Compound	G	R ¹	R ⁴	R ⁵	m.p. (°C)
13	S(O) ₂	C(O)OiPr	H	CH ₂ C(O)OiPr	oil ^k
14	S(O) ₂	C(O)OiPr	H	nPr	oil ^l

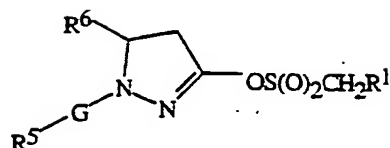
- k ^1H NMR (CDCl_3) δ 8.0 (d,1H), 6.4 (d,1H), 5.15 (m,1H), 5.05 (m,1H), 4.46 (s,2H), 4.41 (s,2H), 1.32 (dd,6H), 1.22 (d,6H).

- l ^1H NMR (CDCl_3) δ 8.0 (d,1H), 6.4 (d,1H), 5.15 (m,1H), 4.47 (s,2H), 3.45 (t,2H), 1.75 (m,2H), 1.31 (d,6H), 1.04 (t,3H).
- 15

Index Table D

Compound	G	R ¹	R ³	R ⁵	m.p. (°C)
15	S	C(O)OMe	CH ₃	iBu	oil ^m
16	S(O)	C(O)OMe	CH ₃	iBu	oil ⁿ

- m ^1H NMR (CDCl_3) δ 1.0 (d,3H), 1.9 (m,1H), 3.09 (d,2H), 3.70 (s,3H), 3.85 (s,3H), 4.65 (s,2H).
- n ^1H NMR (CDCl_3) δ 1.16 (t,3H), 2.21-2.44 (m,1H), 3.01-3.12 (m,1H), 3.30-3.40 (m,1H), 3.88 (s,1H), 4.17 (s,3H), 4.63 (s,2H).
- 20

Index Table E

<u>Compound</u>	<u>G</u>	<u>R¹</u>	<u>R⁶</u>	<u>R⁵</u>	<u>m.p. (°C)</u>
17	C(O)	C(O)OMe	H	N(H)nPr	oil ^o
18	C(O)	C(O)OMe	CH ₃	N(H)iPr	oil ^P

^o ¹H NMR (CDCl₃) δ 0.9 (m,4H), 1.2-1.8 (m,4H), 3.2 (m,2H), 3.8 (m,2H), 3.9 (s,2H), 4.4 (m,1H).

5 ^P ¹H NMR (CDCl₃) δ 1.1-2.5 (m,9H), 2.0-3.7 (m,2H), 3.9 (s,3H), 4.1 (m,1H), 4.7 (m,2H), 5.1 (m,1H).

TEST ASouthern Corn Rootworm

10 Test units, each consisting of an 8 ounce (230 mL) plastic cup containing a one-inch square (2.54 cm²) of a wheatgerm diet, were prepared. Solutions of each of the test compound in 75/25 acetone/distilled water solvent were sprayed into the tray and cup. Spraying was accomplished by passing the tray and cup, on a conveyer belt, directly beneath a flat fan hydraulic nozzle which discharged the spray at a rate of 0.5 pounds of active ingredient per acre (about 0.55 kg/ha) at 30 p.s.i. (207 kPa). After the spray on 15 the cups had dried, five second-instar larvae of the southern corn rootworm (*Diabrotica undecimpunctata howardi*) were placed into each cup. The cups were then held at 27°C and 50% relative humidity for 48 hours, after which time mortality readings were taken. The same units were read again at 6 days later. Of the compounds tested, 80% or greater control was achieved using the following compounds: 1, 2, 3, 4, 13, 14*, 20 15 and 16.

* - tested at 250 ppm.

TEST BAster Leafhopper

25 Test units were prepared from a series of 12 ounce (350 mL) cups, each containing oat (*Avena sativa*) seedlings in a 1 inch (2.54 cm) layer of sterilized soil. The test units were sprayed as described in TEST A with individual solutions of the test compounds. After the oats had dried from the spraying, between 10 and 15 adult aster leafhoppers (*Mascrostes fascifrons*) were aspirated into each of the cups. The cups were covered with vented lids and held at 27°C and 50% relative humidity for 48 hours, after which 30 time mortality readings were taken. Of the compounds tested, 80% or greater control

was achieved using the following compounds: 1, 4, 14*, 15 and 16.

* - tested at 250 ppm.

TEST C

Two-Spotted Spider Mite

- 5 One inch squares (2.54 cm) of kidney bean leaves that had been infested on the undersides with 25 to 30 adult mites (*Tetranychus urticae*) were sprayed with their undersides facing up on a hydraulic sprayer with a solution of the test compounds in 75/25 acetone/distilled water solvent. Spraying was accomplished by passing the leaves, on a conveyor belt, directly beneath a flat fan hydraulic nozzle which discharged the
- 10 spray at a rate of 0.55 pounds of active ingredient per acre (about 0.5 kg/ha) at 30 p.s.i. (207 kPa). The leaf squares were then placed underside-up on square of wet cotton in a petri dish and the perimeter of the leaf square was tamped down onto the cotton with forceps so that the mites cannot escape onto the untreated leaf surface. The test units were held at 27°C and 50% relative humidity for 48 hours, after which time
- 15 mortality readings were taken. Of the compounds tested, 80% or greater control was achieved using the following compound: 4.

TEST D

Boll Weevil

- 20 Five adult bollweevils (*Anthonomus grandis grandis*) were placed into each of a series of 9 ounce (260 mL) cups. The test units were sprayed as described in TEST A with individual solutions of the test compounds. Each cup was then covered with a vented lid and held at 27°C and 50% relative humidity for 48 h, after which time mortality readings were taken. Of the compounds tested, 80% or greater control was achieved using the following compound: 16.

25

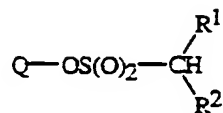
TEST E

Black Bean Aphid

- Individual nasturtium leaves were infested with 10-15 aphids (all stages of *Aphis fabae*) and sprayed with their undersides facing up as described in TEST A. The leaves were then set in 3/8 inch (0.94 cm) diameter vials containing 4 mL of sugar water
- 30 solution and covered with a clear plastic 1 ounce (29 mL) portion cup to prevent escape of aphids that drop from the leaves. The test units were held at 27°C and 50% relative humidity for 48 h, after which time mortality readings were taken. Of the compounds tested, 80% or greater control was achieved using the following compounds: 15 and 16.

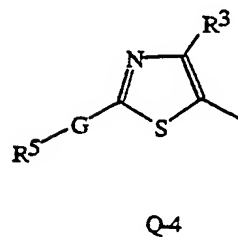
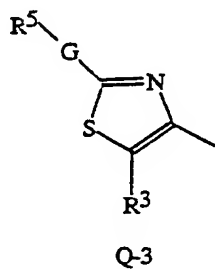
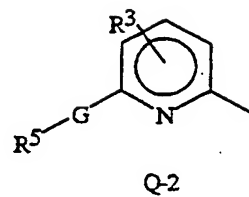
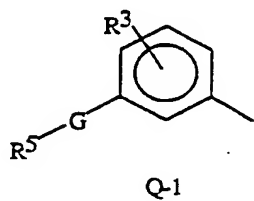
CLAIMS

1. A compound of the formula

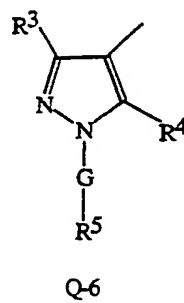
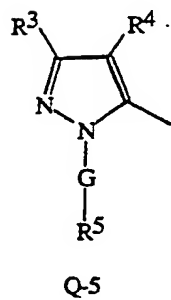


5 wherein:

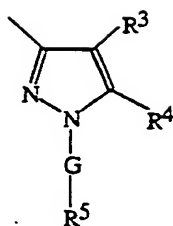
Q is selected from the group



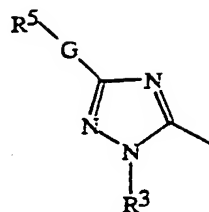
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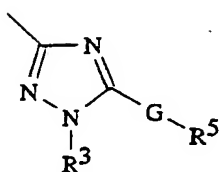
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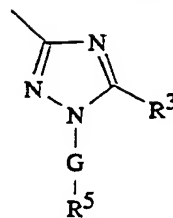
Q-7



Q-8

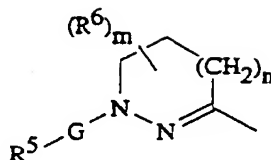


Q-9



Q-10

and



Q-11

- 5 R^1 is selected from the group CN, NO_2 , OR^7 , $C(O)R^7$, $C(O)OR^7$, $C(O)N(R^7)R^8$, SR^7 , $S(O)R^7$, $S(O)_2R^7$ and $S(O)_2N(R^7)R^8$;
- R^2 is selected from the group H, C_1 - C_3 alkyl, CN, $C(O)OR^7$ and $C(O)N(R^7)R^8$;
- R^3 and R^4 are independently selected from the group C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy, C_1 - C_6 haloalkoxy, C_1 - C_6 alkylthio, C_1 - C_6 haloalkylthio, C_1 - C_6 alkylsulfinyl, C_1 - C_6 haloalkylsulfinyl, C_1 - C_6 alkylsulfonyl, C_1 - C_6 haloalkylsulfonyl, C_2 - C_6 alkenyl, C_2 - C_6 alkenyloxy, C_2 - C_6 haloalkenyl, C_2 - C_6 haloalkenyloxy, C_2 - C_6 alkenylthio, C_2 - C_6 haloalkenylthio, C_2 - C_6 alkenylsulfinyl, C_2 - C_6 haloalkenylsulfinyl, C_2 - C_6 alkenylsulfonyl, C_2 - C_6 haloalkenylsulfonyl, C_2 - C_6 alkynyl, C_2 - C_6 alkynyloxy, C_2 - C_6 alkynyloxy, C_2 - C_6 haloalkynyl, C_2 - C_6 alkynylthio, C_2 - C_6 haloalkynylthio, C_2 - C_6 alkynylsulfinyl, C_2 - C_6 haloalkynylsulfinyl, C_2 - C_6 alkynylsulfonyl, C_2 - C_6 haloalkynylsulfonyl, C_3 - C_6 cycloalkyl, C_3 - C_6 halocycloalkyl, C_3 - C_6 cycloalkoxy, C_3 - C_6 halocycloalkoxy, C_3 - C_6 cycloalkylthio, C_3 - C_6 halocycloalkylthio, C_3 - C_6 cycloalkylsulfinyl, C_3 - C_6 halocycloalkylsulfinyl, C_3 - C_6 cycloalkylsulfonyl, C_3 - C_6 halocycloalkylsulfonyl, C_5 - C_6 cycloalkenyl, C_5 - C_6 halocycloalkenyl, C_5 - C_6 cycloalkenyloxy, C_5 - C_6 halocycloalkenyloxy, C_5 - C_6 cycloalkenylthio,

- C₅-C₆ halocycloalkenylthio, C₅-C₆ cycloalkenylsulfinyl,
 C₅-C₆ halocycloalkenylsulfinyl, C₅-C₆ cycloalkenylsulfonyl and
 C₅-C₆ halocycloalkenylsulfonyl each optionally substituted with a substituent
 selected from the group R⁹; H; CN; NO₂; halogen; C₂-C₆ alkylcarbonyl;
 5 C₂-C₆ haloalkylcarbonyl; C₂-C₆ alkoxy carbonyl; C₂-C₆ haloalkoxy carbonyl;
 C(O)N(R¹⁰)R¹¹; C(S)N(R¹⁰)R¹¹; S(O)₂N(R¹⁰)R¹¹; C(O)H; N(R¹⁰)R¹¹;
 phenyl optionally substituted with 1 or 2 substituents independently selected
 from the group W; benzyl optionally substituted with 1 or 2 substituents
 independently selected from the group W;
- 10 R⁵ is selected from the group C₁-C₆ alkyl, C₃-C₆ cycloalkyl, C₂-C₆ alkenyl and
 C₂-C₆ alkynyl each optionally substituted with a substituent selected from
 the group R⁹; C₁-C₆ haloalkyl; C₃-C₆ halocycloalkyl; C₂-C₆ haloalkenyl;
 C₂-C₆ haloalkynyl; C₄-C₇ cycloalkylalkyl; C₄-C₇ halocycloalkylalkyl; and
 N(R¹⁰)R¹¹;
- 15 R⁶ is selected from the group halogen, CN, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₃-C₆
 cycloalkyl, C₂-C₆ alkenyl, C₂-C₆ alkynyl, C₁-C₆ alkoxy, C₃-C₆
 halocycloalkyl, C₂-C₆ haloalkenyl, C₂-C₆ haloalkynyl, C₄-C₇ cycloalkylalkyl,
 C₂-C₆ alkoxy carbonyl, N(R¹⁰)R¹¹, C(O)N(R¹⁰)R¹¹ and phenyl optionally
 substituted with 1 or 2 substituents independently selected from the group
 20 W;
- R⁷ and R⁸ are independently selected the group C₁-C₆ alkyl, C₁-C₆ haloalkyl,
 C₃-C₆ cycloalkyl, phenyl optionally substituted with 1 or 2 substituents
 independently selected from the group W and benzyl optionally substituted
 with 1 or 2 substituents independently selected from the group W;
- 25 R⁹ is selected from the group CN, SCN, NO₂, OH, OR¹², SR¹², S(O)R¹²,
 S(O)₂R¹², OC(O)R¹², OS(O)₂R¹², Si(R¹²)(R¹³)(R¹⁴), C(O)OR¹²,
 C(O)N(R¹²)R¹³, C(O)R¹², N(R¹⁰)R¹¹ and phenyl optionally substituted
 with 1 or 2 substituents independently selected from the group W; provided
 that when R⁹ is S(O)R¹², S(O)₂R¹² or OS(O)₂R¹², R¹² is other than H;
- 30 R¹⁰ is selected from the group C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₁-C₅ alkoxy, C₂-C₅
 alkoxyalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₃-C₆
 haloalkynyl, C₃-C₆ cycloalkyl and C₄-C₇ cycloalkylalkyl each optionally
 substituted with a substituent selected from the group R⁹; N(R¹⁰)R¹¹; phenyl
 optionally substituted with 1 or 2 substituents independently selected from
 35 the group W; benzyl optionally substituted with 1 or 2 substituents
 independently selected from the group W;

R¹¹ is selected from the group H, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C(O)H, C₂-C₃ alkylcarbonyl, C₂-C₃ alkoxy carbonyl, C₂-C₆ alkenyl and C₂-C₆ alkynyl; or

R¹⁰ and R¹¹ are taken together to form a member selected from the group
 5 -CH₂CH₂CH₂CH₂CH₂-, -CH₂CH₂CH₂CH₂- and -CH₂CH₂OCH₂CH₂-;

R¹² is selected from the group H, C₁-C₃ alkyl and C₁-C₃ haloalkyl;

R¹³ and R¹⁴ are independently selected from the group C₁-C₃ alkyl and C₁-C₃ haloalkyl;

G is selected from the group C(O), C(S), S, S(O) and S(O)₂;

10 W is selected from the group halogen, NO₂, CN, C₁-C₃ alkyl, C₁-C₃ haloalkyl, C₁-C₃ alkylthio, C₁-C₃ alkoxy, C₁-C₃ haloalkoxy, C₂-C₄ alkylcarbonyl and C₂-C₄ alkoxy carbonyl;

m is 0, 1, 2, 3, 4, 5 or 6; and

n is 0 or 1.

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2. A compound according to Claim 1

wherein:

R¹ is selected from the group CN and C(O)OR⁷;

R² is H;

20 R³ and R⁴ are independently selected from the group H, halogen, CN, C₁-C₂ alkyl, C₁-C₂ haloalkyl, C₁-C₂ alkoxy and C₁-C₂ alkylthio;

R⁵ is selected from the group C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ haloalkyl, C₂-C₆ haloalkenyl and N(R¹⁰)R¹¹;

R⁹ is selected from the group CN and OR¹²; and

25 G is selected from the group C(O), S, S(O) and S(O)₂.

3. A compound according to Claim 2 wherein Q is Q-2.

4. A compound according to Claim 2 wherein Q is Q-7.

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5. A compound according to Claim 2 wherein Q is Q-8.

6. A compound according to Claim 2 wherein Q is Q-10.

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7. A compound according to Claim 2 wherein Q is Q-11.

8. A compound according to Claim 4 which is:

methyl [[[1-(propylsulfonyl)-1H-pyrazol-3-yl]oxy]sulfonyl]acetate.

9. An arthropodicial composition comprising an arthropodically effective amount of a compound according to Claim 1 and a carrier therefor.
- 5
10. A method for controlling arthropods comprising contacting the arthropods or their environment with an arthropodically effective amount of a compound according to Claim 1.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 94/06346

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C07D231/20 C07D213/81 C07D213/70 C07D231/08 C07D249/12
A01N43/40 A01N43/56 A01N43/653 A01N43/78

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	WO,A,93 10096 (E.I. DU PONT DE NEMOURS AND COMPANY) 27 May 1993 see the whole document ---	1-3,9,10
A	EP,A,0 220 857 (NIPPON KAYAKU KABUSHIKI KAISHA) 6 May 1987 cited in the application see the whole document -----	1-3,9,10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 94/06346

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